

Emergence of half-metallicity in suspended NiO chains: *Ab initio* electronic structure and quantum transport calculations

David Jacob,* J. Fernández-Rossier, and J. J. Palacios

Departamento de Física Aplicada and Instituto Universitario de Materiales de Alicante (IUMA), Universidad de Alicante, 03690 San Vicente del Raspeig, Spain

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Contrary to the antiferromagnetic and insulating character of bulk NiO, one-dimensional chains of this material can become half metallic due to the lower coordination of their atoms. Here we present *ab initio* electronic structure and quantum transport calculations of ideal infinitely long NiO chains and of more realistic short ones suspended between Ni electrodes. While infinite chains are insulating, short suspended chains are half-metallic minority-spin conductors that displays very large magnetoresistance and a spin-valve behavior controlled by a single atom.

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In going from bulk to lower dimensions material properties often change drastically. A recent example is that of interfaces between different insulators which can actually be metallic.¹ Even more recently, it has been predicted theoretically that certain oxygen surfaces of some insulating ceramic oxides can exhibit magnetism and half-metallicity.² The ultimate limit in this respect can be found in atomic chains formed in metallic nanocontacts that allow one to study the transport properties of one-dimensional systems of atomic size.³ Due to the lower coordination of the atoms the properties of metallic atomic chains formed in nanocontacts can be remarkably different from those in the bulk. For example, Pt nanocontacts can exhibit magnetic order when atomic chains are formed.⁴ More complex one-dimensional systems like carbon-cobalt atomic chains⁵ or organometallic benzene-vanadium wires⁶ have even been predicted to be half-metallic conductors.

However, not all metals form atomic chains in nanocontacts, although recently it has been found that the presence of oxygen favors their formation.⁷ For example, experiments with Ni nanocontacts^{8,9} have never shown evidence of chain formation. Nevertheless, the presence of oxygen in the contact region could possibly lead to the formation of NiO chains. In this context it has also been proposed that the rather moderate magnetoresistive properties of pure Ni nanocontacts^{10,11} could be enhanced considerably by the presence of oxygen adsorbates on the surface of the Ni electrodes.¹² On the other hand, bulk NiO is a common example of a correlated insulator with antiferromagnetic (AF) order (see, e.g., Refs. 13 and 14), which remains insulating even above the Néel temperature when the AF order is lost. Thus it is not at all obvious whether or not oxidized Ni nanocontacts or NiO chains should be conductors.

In this Rapid Communication we investigate the electronic and magnetic structure and the transport properties of one-dimensional NiO chains, both idealized infinite ones and more realistic short ones suspended between Ni nanocontacts. Anticipating our most important results, our *ab initio* quantum transport calculations show that short NiO chains suspended between Ni nanocontacts can become half-metallic conductors, i.e., carry an almost 100% spin-polarized current. This result holds true even for a single O

atom in between Ni electrodes. Consequently, for antiparallel alignment of the electrode magnetizations the transport through the contact is strongly suppressed, resulting in a very large magnetoresistance (MR) [difference in resistance between antiparallel and parallel alignments of the magnetizations of the electrodes normalized either to the higher resistance value (MR_1) or to the lower one (MR_2): $MR_1 \approx 90\%$ and $MR_2 \approx 700\%$, respectively].

The electronic structures of both idealized infinitely long NiO chains and the more realistic short suspended chains have been calculated in the density functional theory (DFT) approximation using the hybrid functional B3LYP,¹⁵ which combines local and nonlocal exchange. This functional has been successful in describing the electronic and magnetic structures of some strongly correlated materials like bulk NiO. In particular, it describes very well the charge-transfer character, the magnitude of the gap and the magnetic moment of NiO, and predicts the correct AF order.¹⁴ It is important to stress here that due to the insufficient cancellation of the self-interaction in the local exchange functional of the local density approximation (LDA) the occupied narrow $3d$ bands are raised in energy. As a result the LDA severely underestimates the gap of bulk NiO.¹⁶ The generalized gradient approximation (GGA) to the exchange functional improves somewhat the description of NiO but the energy gap of ~ 2 eV is still too small and also the charge-transfer character is not captured correctly.¹⁶ The B3LYP functional corrects the self-interaction error inherent in the LDA and GGA by mixing the exact nonlocal Hartree-Fock (HF) exchange with the GGA exchange functional. The DFT-based alternatives that correct the self-interaction error, like LDA+ U , the self-interaction-corrected LDA, and the GW approximation lead to results similar to those obtained from the B3LYP.¹⁴

The electronic structure of infinite NiO chains has been calculated with the CRYSTAL03 program package¹⁷ while for the electronic structure and quantum transport calculations of the suspended chains we have used our *ab initio* quantum transport package ALACANT.^{18,19} The infinite chain-calculations were done with elaborate all-electron basis sets for Ni and O,^{20,21} similar to those employed for reported HF and B3LYP calculations of bulk NiO,¹⁴ but extended with a diffusive sp function in the case of Ni and a d polarization

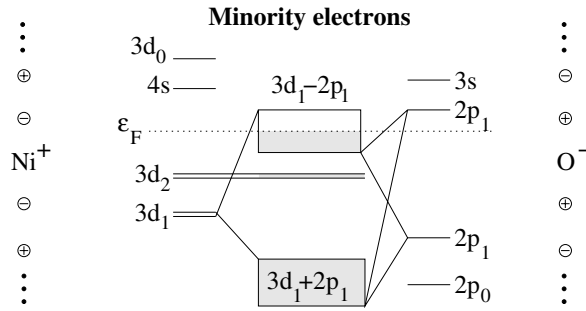


FIG. 1. Schematic one-electron energies of a one-dimensional NiO chain in the z direction for minority spin. To the left and right the orbital energies of an individual Ni^+ cation and an O^- anion in the crystal field of a one-dimensional Ni^+O^- chain are shown. In the center the formation of valence and conduction bands by hybridization of Ni $3d$ and O $2p$ orbitals is shown.

function in the case of O. Using these basis sets we reproduce the B3LYP results for bulk NiO.¹⁴ We have also employed minimal basis sets with effective core pseudopotentials described in earlier work¹⁰ for both Ni and O, and have found that the results change very little. Thus we have employed these minimal basis sets for the more demanding transport calculations.

The electronic properties of NiO are, to a large extent, determined by atomic scale properties, like the crystal field splitting of the Ni and O energy levels and the amount of electron charge transferred from Ni to O. The latter, in turn, is determined by the interplay between the Madelung binding energy, the ionization potential of Ni, and the electron affinity of O. Due to the lower coordination and the corresponding decrease in Madelung binding energy the electron transfer from Ni to O is less favorable in an atomic chain than in bulk (where the electron transfer is almost complete, resulting in an ionic configuration of $\text{Ni}^{2+}\text{O}^{2-}$). The proper starting point to discuss the formation of energy bands in the one-dimensional NiO chain is therefore the univalent ions Ni^+ and O^- .

In order to understand how the low coordination affects the atomic properties of the constituting ions we have first performed B3LYP calculations of both a single Ni^+ ion and a single O^- ion, each in the field of point charges that mimic the crystal field of a one-dimensional chain of univalent Ni and O ions. We find that for both ions the spin-doublet state ($S=1/2$) minimizes the energy as is the case for the free ions. In Fig. 1 we show schematically the energy levels of Ni^+ and O^- in the presence of the point charges for minority spin only. Interestingly, for minority spins, the occupied Ni $3d_1$ orbitals (d_{xz} and d_{yz}) of the Ni^+ ion fall energetically in between the occupied and unoccupied O $2p_1$ orbitals (p_x and p_y) of the O^- ion. Thus the $3d_1$ and $2p_1$ orbitals can form two filled degenerate bonding bands and two degenerate partially filled antibonding bands as indicated in the middle part of Fig. 1. The $3d_2$ (d_{xy} and $d_{x^2-y^2}$) doublet is somewhat above the $3d_1$ but cannot hybridize with the oxygen $2p$ orbitals. The Ni $3d_0$ ($d_{3z^2-r^2}$) and $4s$ are empty in energy while the O $2p_0$ (p_z) and $2s$ orbitals are filled and much lower in energy so that no hybridization takes place, though symmetry would allow for it.

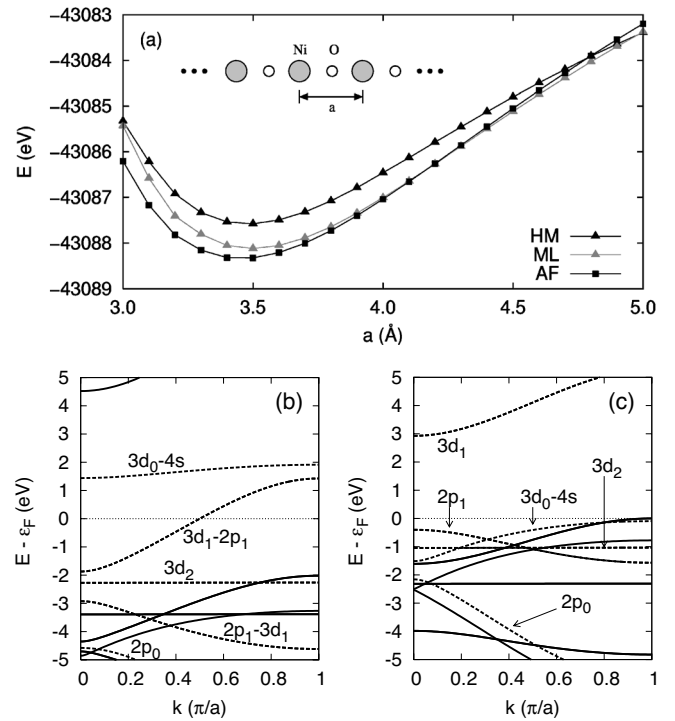


FIG. 2. (a) Energy per unit cell on the infinite NiO chain in dependence on the lattice spacing a . Black triangles indicate the half-metallic state (HM), gray triangles the moleculelike insulating state with FM order (ML), and black boxes the insulating state with AF order (AF). (b) Band structure of HM state for a lattice spacing of 3.6 Å. Solid lines indicate majority-spin bands and dashed lines indicate minority-spin bands. (c) Same as (b) but for ML FM state.

On the other hand, for majority-spin electrons (not shown) all five Ni $3d$ orbitals are filled while the $4s$ is also empty, i.e., the Ni^+ valence configuration is $3d^9$ and not $4s^1 3d^8$ as for the free Ni^+ ion. Moreover, all of the O $2p$ orbitals are filled so that the Ni^+ and O^- ions can form only either completely filled or completely empty bands for the majority spin. Thus the ionic picture suggests that a one-dimensional NiO chain should become a half-metallic conductor where only one kind of spin level forms the conducting bands. In this case only the minority-spin $3d_1$ bands would conduct so that, according to the proposed classification in Ref. 22, it would be of type I_B .

Not surprisingly, our calculations for infinite one-dimensional NiO chains (Fig. 2) show that a univalent ionic configuration as an initial guess results in a half-metallic state for large separation of the individual chain atoms (i.e., large lattice spacing of 5 Å) as suggested by the ionic picture. However, as can be seen from Fig. 2(a), the half-metallic state is only a metastable state for most values of the lattice spacing. This half-metallic state is “shadowed” by a second state with ferromagnetic (FM) order and insulating character. By successively decreasing the lattice spacing a of the chain and using the (half-metallic) state of the previous step for the initial guess, the half-metallic state can be generated also for smaller interatomic distances, which points toward its metastability. Around the equilibrium lattice spacing ($a \sim 3.4$ Å) the ground state of the chain has AF order

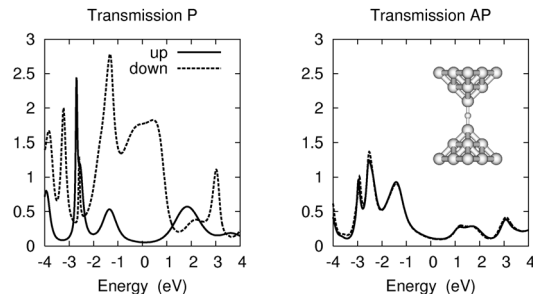


FIG. 3. Transmission per spin channel in the case of P (left) and AP (right) alignment of the electrode magnetizations for NiO chain consisting of one oxygen atom bridging the two Ni tip atoms of the Ni electrodes as shown on the inset in the right panel. The separation of the two Ni tip atoms is 3.6 Å.

and is of insulating character with a substantial gap of ~ 4 eV as in the bulk. When stretched out of equilibrium the FM state and the AF state become comparable in energy until finally, at a lattice spacing of ~ 4.2 Å, the FM state becomes the ground state.

The band structure diagram in Fig. 2(c) shows that the metastable state with FM order corresponds indeed to the half-metallic state suggested by the ionic picture. The half-filled doubly degenerate conduction band is formed by minority-spin Ni $3d_1$ orbitals hybridized with O $2p_1$ orbitals while the Ni $3d_2$ orbitals do not hybridize with O $2p$ orbitals and thus form a flat valence band. The lowest-lying empty band is formed by the minority-spin Ni $3d_0$ orbital, which is slightly hybridized with the Ni $4s$ orbital. On the other hand the stable state with FM order and insulating character [see the band structure in Fig. 2(b)] actually corresponds to the ground state of the NiO molecule, which is a ${}^3\Sigma^{-1}$ state.²³ The main difference from the half-metallic state is that now the nondegenerate Ni $3d_0$ and $4s$ orbitals form a minority-spin valence band while the minority-spin doubly degenerate half-filled antibonding band composed of Ni $3d_1$ and O $2p_1$ bands is emptied and a substantial gap of ~ 3 eV opens. Thus the infinite chain behaves like an insulator for reasonable values of the chain stretching.

Atomic chains formed in break junctions have a finite length and are suspended between electrodes. It is well known that the contact between the atomic chain and the electrode tip will have considerable effect on the electronic structure of the chain, especially when d orbitals are involved, as is the case here.¹⁰ We have thus calculated the electronic structure and transport properties of both a single oxygen atom and a O-Ni-O chain bridging the two tips of a Ni nanocontact as shown in the insets of the right panels of Figs. 3 and 4. In the case of the single oxygen atom (Fig. 3) the electron transport is almost 100% spin polarized around the Fermi level for parallel (P) alignment of the magnetizations of the two Ni electrodes. Moreover, an orbital eigenchannel analysis²⁴ reveals that the transport is mainly due to two almost perfectly transmitting minority-spin channels composed of Ni $3d_1$ and O $2p_1$ orbitals, i.e., they correspond to the doubly degenerate conduction band of the metastable half-metallic state in the perfect chain. Thus the half-metallic state which was suppressed in the idealized case of the infi-

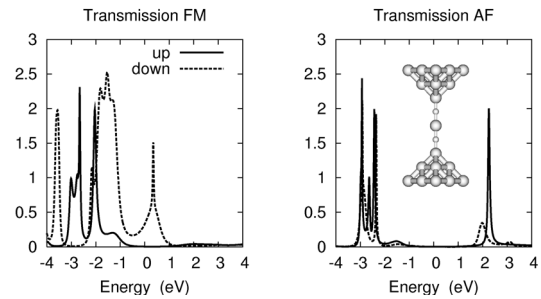


FIG. 4. Transmission per spin channel for suspended chain consisting of a O-Ni-O bridge and the Ni tip atoms shown in inset of right panel in the case of FM order (left) and of AF order (right). For AF order the magnetization of the Ni atom in the center of the chain is reversed with respect to the two Ni tip atoms. Distance between a Ni tip atom and the center atom is 3.6 Å.

nite chain emerges in the more realistic situation of a short suspended chain. We can understand this phenomenon in terms of the orbital blocking mechanism proposed earlier in the context of Ni nanocontacts.^{10,24} The highest minority-spin valence band of the insulating state with FM order in the infinitely long chain has a strong contribution from the Ni $3d_0$ orbital that is not compatible with the geometry of the pyramid-shaped Ni contacts, so that this band is blocked and thus cannot be occupied. Instead, the doubly degenerate band composed of Ni $3d_1$ orbitals hybridized with O $2p_1$ orbitals is partially filled, resulting in the half-metallic state which in the perfect chain is only metastable. Thus the orbital blocking by the contacts actually turns the chain into a half-metallic conductor. Consequently, the conductance is strongly suppressed in the case of antiparallel (AP) alignment of the magnetizations of the Ni electrodes, as can be seen from the right panel of Fig. 3, and the MR becomes very large: $MR_1 \approx 90\%$ and $MR_2 \approx 700\%$.

Varying the distance d between the Ni tip atoms leads to results similar to those shown in Fig. 3. For the P case the current through the chain is almost 100% spin polarized with two open minority channels composed of Ni $3d_1$ and O $2p_1$ orbitals, while for the AP case it is strongly suppressed, resulting in very high MR values between 80% and 90% for MR_1 for d between 3.0 and 5.0 Å. Geometry relaxations for different values of the tip-tip distance show that for small distances the oxygen atom goes into a zigzag position. The bonding angle decreases with increasing distance until it becomes zero at 3.6 Å. Finally, the chain breaks for $d > 4.8$ Å. Thus the scattering is strong for small distances $d < 3.6$ Å when the bonding angle is appreciable and for large stretching, $d > 4.2$ Å, resulting in a considerable reduction in the conduction of the two minority channels.

In longer suspended chains the insulating state with FM order starts to emerge inside the chain and away from the contacts. As a result the conductance is reduced, as can be seen already in the case of the O-Ni-O bridge (Fig. 4). The minority-spin conduction is reduced considerably ($\sim 30\%$) compared to the case of the single oxygen bridge. On the other hand the conduction of the majority-spin channel becomes practically zero ($< 0.2\%$). This can be understood by the fact that the residual majority-spin channel conductance

of the single oxygen bridge is due to direct hopping of Ni *s* electrons between the electrodes and therefore vanishes when the distance between the electrodes is large. The finite minority-spin conductance opens up the possibility of an interesting phenomenon: When the middle Ni atom reverses its spin, the conductance drops to nearly zero (see right panel of Fig. 4) since the AF chain is insulating. In other words, this system behaves as a single-atom spin valve that presents an extremely large MR, even higher than that reported above for the single oxygen bridge: $MR_1 \approx 99\%$ and $MR_2 \approx 10\,000\%$. Apart from controlling the magnetization direction of the central atom by a magnetic field, Fig. 2(a) suggests that a mechanical control of the spin valve (by stretching the chain) would also be possible.

In conclusion, we have shown that one-dimensional infinite NiO chains are insulating and have AF order around the equilibrium lattice spacing but can actually become FM insulators when stretched out of equilibrium, in contrast to bulk NiO. In the more realistic case of a short NiO chain suspended between Ni nanocontacts the chain becomes an almost 100% spin-polarized conductor. The emergence of al-

most perfect half-metallicity (i.e., almost 100% spin polarization of the conduction channel) in suspended chains leads to a strong suppression of the current for AP alignment of the electrodes resulting in very large MR values of $MR_1 \approx 90\%$ and $MR_2 \approx 700\%$, respectively. This could perhaps explain to some extent the very large MR values in Ni nanocontacts obtained in some experiments⁸ where oxygen is likely to be present. Finally, the O-Ni-O bridge suspended between Ni electrodes operates as a single-atom spin valve where the currentflow is controlled by the magnetization of a single atom.

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*Electronic address: david.jacob@ua.es

- ¹A. Ohtomo and H. Y. Hwang, *Nature* (London) **427**, 423 (2004); S. Okamoto and A. J. Millis, *ibid.* **428**, 630 (2004).
- ²S. Gallego, J. I. Beltrán, J. Cerdá, and M. C. Muñoz, *J. Phys.: Condens. Matter* **17**, L451 (2005).
- ³N. Agrait, A. L. Yeyati, and J. M. van Ruitenbeek, *Phys. Rep.* **377**, 81 (2003), and references therein.
- ⁴J. Fernández-Rossier, D. Jacob, C. Untiedt, and J. J. Palacios, *Phys. Rev. B* **72**, 224418 (2005).
- ⁵E. Durgun, R. T. Senger, H. Mehrez, S. Dag, and S. Ciraci, *Europhys. Lett.* **73**, 642 (2006).
- ⁶V. V. Maslyuk, A. Bagrets, T. Bredow, and I. Mertig, *cond-mat/0510144* (unpublished).
- ⁷W. H. A. Thijssen, D. Marjenburgh, R. H. Bremmer, and J. M. van Ruitenbeek, *Phys. Rev. Lett.* **96**, 026806 (2006).
- ⁸N. García, M. Muñoz, and Y. W. Zhao, *Phys. Rev. Lett.* **82**, 2923 (1999); M. R. Sullivan, D. A. Boehm, D. A. Ateya, S. Z. Hua, and H. D. Chopra, *Phys. Rev. B* **71**, 024412 (2005).
- ⁹M. Viret, S. Berger, M. Gabureac, F. Ott, D. Olligs, I. Petej, J. F. Gregg, C. Fermon, G. Francinet, and G. LeGoff, *Phys. Rev. B* **66**, 220401(R) (2002); C. Untiedt, D. M. T. Dekker, D. Djukic, and J. M. van Ruitenbeek, *ibid.* **69**, 081401(R) (2004); Z. K. Keane, L. H. Yu, and D. Natelson, *Appl. Phys. Lett.* **88**, 062514 (2006); K. I. Bolotin, F. Kuemmeth, A. N. Pasupathy, and D. C. Ralph, *Nano Lett.* **6**, 123 (2006).
- ¹⁰D. Jacob, J. Fernández-Rossier, and J. J. Palacios, *Phys. Rev. B* **71**, 220403(R) (2005).
- ¹¹A. Bagrets, N. Papanikolaou, and I. Mertig, *cond-mat/0510073* (unpublished); A. Smogunov, A. DalCorso, and E. Tosatti, *Phys. Rev. B* **73**, 075418 (2006); A. R. Rocha, V. M. Garcia-Suarez, S. Bailey, C. Lambert, J. Ferrer, and S. Sanvito, *ibid.* **73**, 085414 (2006).
- ¹²N. Papanikolaou, *J. Phys.: Condens. Matter* **15**, 5049 (2003).
- ¹³G. A. Sawatzky and J. W. Allen, *Phys. Rev. Lett.* **53**, 2339 (1984).
- ¹⁴I. P. R. Moreira, F. Illas, and R. L. Martin, *Phys. Rev. B* **65**, 155102 (2002).
- ¹⁵A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ¹⁶T. C. Leung, C. T. Chan, and B. N. Harmon, *Phys. Rev. B* **44**, 2923 (1991).
- ¹⁷V. Saunders *et al.*, Computer code CRYSTAL03, Release 1.0.2, Theoretical Chemistry Group, Università Di Torino, Torino, Italy.
- ¹⁸J. J. Palacios, A. J. Pérez-Jiménez, E. Louis, E. SanFabián, and J. A. Vergés, *Phys. Rev. B* **66**, 035322 (2002).
- ¹⁹J. J. Palacios, D. Jacob, A. J. Pérez-Jiménez, E. S. Fabián, E. Louis, and J. A. Vergés, Computer code ALACANT, release 1.0, Condensed Matter Group, Universidad de Alicante, <http://www.guirisystems.com/alacant>
- ²⁰K. Doll, *Surf. Sci.* **544**, 103 (2003).
- ²¹E. Ruiz, M. Llunell, and P. Alemany, *J. Solid State Chem.* **176**, 400 (2003).
- ²²J. M. D. Coey, J. J. Versluijs, and M. Venkatesan, *J. Phys. D* **35**, 2457 (2002).
- ²³K. Doll, M. Dolg, P. Fulde, and H. Stoll, *Phys. Rev. B* **55**, 10282 (1997).
- ²⁴D. Jacob and J. J. Palacios, *Phys. Rev. B* **73**, 075429 (2006).